CERTIFICATION

I, Satoko Yamaguchi, of TOYOTA TECHNICAL DEVELOPMENT CORPORATION, 1-21, Imae, Hanamoto-cho, Toyota, Aichi, 470-0334 Japan, hereby certify that I am the translator of the accompanying certified official copy of the documents in respect of an application for a patent filed in Japan and of the official certificate attached thereto, and certify that the following is a true and correct translation to the best of my knowledge and belief.

Application Number	Date of Filing
Japanese Patent Application No. 2002-346180	November 28, 2002

Satoko Yamaguchi

Satoko Yamaguchi

Dated this 25th day of August, 2006

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application November 28, 2002

Application Number Japanese Patent Application No. 2002-346180

[ST.10/C]: [JP2002-346180]

Applicant(s): TOYOTA JIDOSHA KABUSHIKI KAISHA

June 9, 2003
Commissioner, Japan Patent Office Shinichiro Ohta

[NAME OF THE DOCUMENT] APPLICATION FOR PATENT

[SERIAL NUMBER] P02-0943

[SPECIAL NOTES] Application for patent to be pursuant to provision of Section 30, Paragraph 1 of Patent Law

[FILING DATE] November 28, 2002

[ADDRESSEE] Commissioner of Patent Office

[INT. CL.] C08G 61/10

H01B 1/12

[TITLE OF THE INVENTION] PHOSPHORUS-CONTAINING POLYMER COMPOUND, SYNTHESIZING METHOD THEREOF, HIGH-DURABILITY POLYMER ELECTROLYTE COMPOSITE, AND FUEL CELL

[NUMBER OF CLAIMS] 6

[INVENTOR]

[DOMICILE OR RESIDENCE] c/o TOYOTA JIDOSHA KABUSHIKI KAISHA

1, Toyota-cho, Toyota-shi, Aichi-ken

[NAME] Takumi TANIGUCHI

[INVENTOR]

[DOMICILE OR RESIDENCE] c/o TOYOTA JIDOSHA KABUSHIKI KAISHA

1, Toyota-cho, Toyota-shi, Aichi-ken

[NAME] Masayoshi TAKAMI

[INVENTOR]

[DOMICILE OR RESIDENCE] c/o SOPHIA UNIVERSITY

7-1 Kioi-cho, Chiyoda-ku, Tokyo-to

[NAME]	Masahiro RIKUKAWA
[INVENTOR]	
[DOMICILE OR RESIDENCE]	c/o SOPHIA UNIVERSITY 7-1 Kioi-cho, Chiyoda-ku, Tokyo-to
[NAME]	Yuko TAKEOKA
[APPLICANT]	
[ID NUMBER]	000003207
[NAME]	TOYOTA JIDOSHA KABUSHIKI KAISHA
[LEGAL REPRESENTATIVE]	
[ID NUMBER]	100091096
[PATENT ATTORNEY]	
[NAME]	Yusuke HIRAKI
[DESIGNATED LEGAL REPRESENTATIVE]	
[ID NUMBER]	100102576
[PATENT ATTORNEY]	
[NAME]	Toshiaki WATANABE
[DESIGNATED LEGAL REPRESENTATIVE]	
[ID NUMBER]	100103931
[PATENT ATTORNEY]	
[NAME]	Tsuruhiko SEKIGUCHI
[APPLICATION FEE]	
[PAYMENT NUMBER]	015244

[AMOUNT OF PAYMENT] 21, 000 yen

[LIST OF ATTACHED DOCUMENTS]

[NAME OF THE DOCUMENT]	Specification	1
[NAME OF THE DOCUMENT]	Drawings	1
[NAME OF THE DOCUMENT]	Abstract	1

[REQUIREMENT OF PROOF] Required

[NAME OF THE DOCUMENT] SPECIFICATION

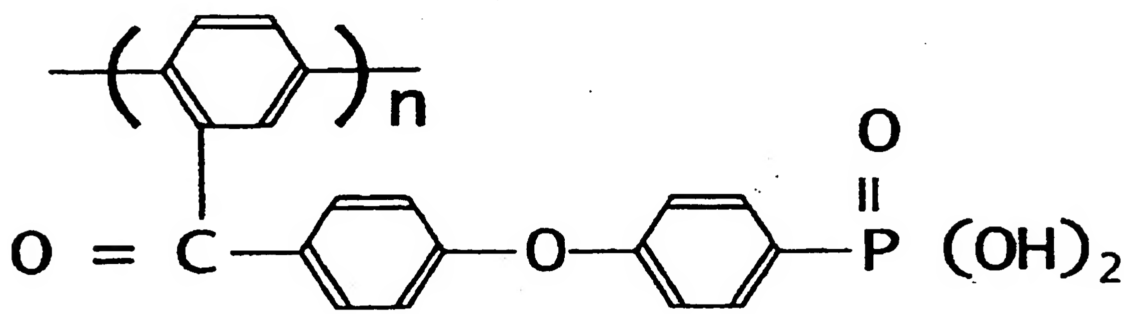
[TITLE OF THE INVENTION] PHOSPHORUS-CONTAINING POLYMER COMPOUND, SYNTHESIZING METHOD THEREOF, HIGH-DURABILITY POLYMER ELECTROLYTE COMPOSITE, AND FUEL CELL

[CLAIMS]

[CLAIM 1]

Phosphonated poly (4-phenoxybenzoyl-1,4-phenylene) having a following repeating unit.

(Chemical formula 1)



(It is to be noted in the above formula that "n" represents a number of 5 to 10000.)

[CLAIM 2]

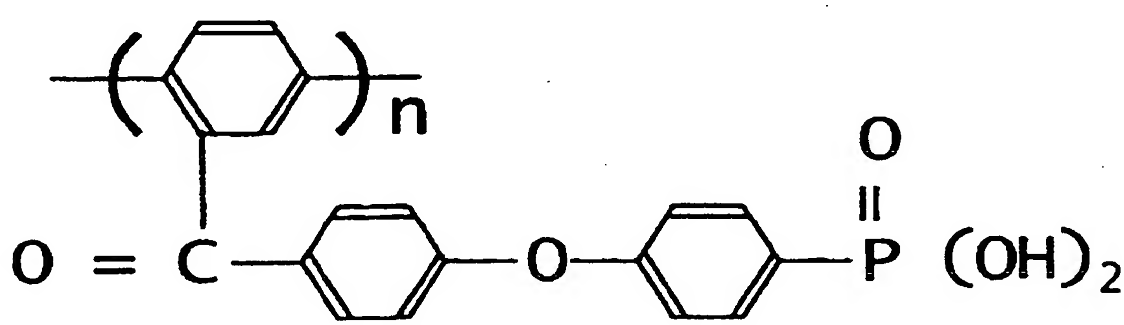
A method for synthesizing phosphonated poly (4-phenoxybenzoyl-1,4-phenylene) having a following repeating unit, comprising:

halogenating a phenoxy group of the poly (4-phenoxybenzoyl-1,4-phenylene);

phosphonic acid esterifying the halogen group; and

deesterifying the phosphonic acid ester group.

(Chemical formula 2)

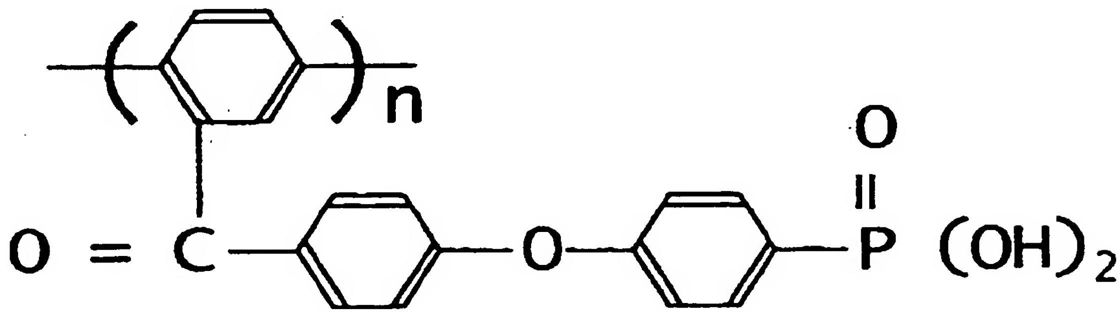


(It is to be noted in the above formula that "n" represents a number of 5 to 10000.)

[CLAIM 3]

An antioxidant including phosphonated poly (4-phenoxybenzoyl-1,4-phenylene) having a following repeating unit.

(Chemical formula 3)

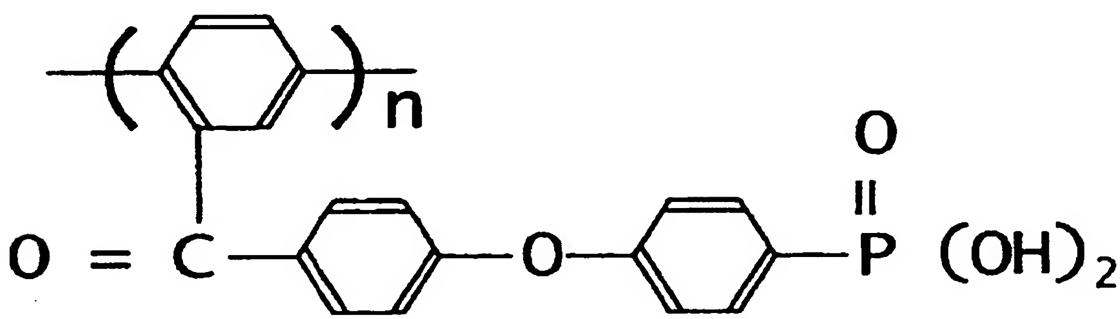


(It is to be noted in the above formula that "n" represents a number of 5 to 10000.)

[CLAIM 4]

A high-durability polymer electrolyte composite including a fluoropolymer electrolyte and the phosphonated poly (4-phenoxybenzoyl-1,4-phenylene) having a following repeating unit.

(Chemical formula 4)



(It is to be noted in the above formula that "n" represents a number of 5 to 10000.)

[CLAIM 5]

An electrode for a fuel cell, which includes a proton exchange material and a catalyst support conductive material, characterized in that the proton exchange material is a high-durability polymer electrolyte composite including a fluoropolymer electrolyte and the phosphonated poly (4-phenoxybenzoyl-1,4-phenylene).

[CLAIM 6]

A fuel cell comprising the electrode according to claim 5.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[TECHNICAL FIELD]

The invention relates to a novel phosphorus-containing polymer compound, a method for synthesizing the phosphorus-containing polymer compound, a high-durability polymer electrolyte composite including the phosphorus-containing polymer compound and a fluoropolymer electrolyte, and a high-durability fuel cell.

[0002]

[RELATED ART]

Various types of antioxidants to be added to various sorts of organic materials have been developed. For example, a phenol compound, an amine compound, a sulfur compound, and a compound containing phosphorus are known. Also, not only low molecular weight antioxidants but also high molecular weight antioxidants have been developed. However, in order to apply an antioxidant to a polymer electrolyte or the like for a fuel cell, it is desired that a polymer antioxidant be developed whose outflow to the outside of a system of the fuel cell is small even in a humid condition, which has higher heat resistance, and which can maintain performance of the fuel cell for a long time.

[0003]

Meanwhile, a polymer electrolyte is a solid polymer material having an electrolytic functional group such as a sulfonic acid group in a polymer chain thereof. The polymer electrolyte is strongly bonded to a certain ion, and is selectively pervious to a positive ion or a negative ion. Therefore, the polymer electrolyte is formed as particles, fiber or membranes, and is applied to various uses such as electrodialysis, diffusion dialysis and battery diaphragms.

[0004]

For example, a reformed gas fuel cell has a proton conductive polymer electrolyte membrane with one electrode provided on each surface thereof. In the reformed gas fuel cell, hydrogen gas, which is obtained by reforming a low molecular weight hydrocarbon such as methane and methanol, is supplied to one of the electrodes (fuel electrode) as fuel gas, while oxidizing gas or air is supplied to the other electrode (air electrode) as an oxidant, such that an electromotive force is generated. Water electrolysis is a method for generating hydrogen and oxygen by electrolyzing water using a polymer electrolyte membrane.

[0005]

In the case of a fuel cell or water electrolysis, a peroxide is generated in a catalyst layer formed on an interface between the polymer electrolyte membrane and the electrode, and the generated peroxide becomes a peroxide radical while being diffused, and causes a reaction which deteriorates the polymer electrolyte membrane. Therefore, it is difficult to use a hydrocarbon polymer electrolyte membrane having low oxidation resistance. Accordingly, in the fuel cell and water electrolysis, a perfluoro sulfonic acid membrane having high proton conductivity, and high oxidation resistance is generally used.

[0006]

Salt electrolysis is a method for generating sodium hydroxide, chlorine, and hydrogen by electrolyzing a sodium chloride solution using a polymer electrolyte membrane. In this case, the polymer electrolyte membrane is exposed to chloride, and a high-temperature solution containing a high concentration of sodium hydroxide. Therefore, it is impossible to use a hydrocarbon polymer electrolyte membrane having low resistance to chloride, and the high-temperature and concentrated sodium hydroxide solution. Accordingly, a polymer electrolyte membrane for salt electrolysis, e.g., a perfluoro sulfonic acid membrane, is generally used which is resistant to chlorine and a high-temperature and concentrated sodium hydroxide solution. A carboxylic acid group may be partially introduced to a surface of the perfluoro sulfonic acid membrane in order to prevent back-diffusion of generated ions.

[0007]

A fluoropolymer electrolyte membrane typified by the perfluoro sulfonic acid membrane has C-F bonding and therefore has a considerably high chemical stability. Accordingly, the fluoropolymer electrolyte is used not only as a polymer electrolyte membrane for a fuel cell, water electrolysis or salt electrolysis, but also as a polymer electrolyte membrane for hydrohalic acid electrolysis. Also, the fluoropolymer electrolyte is widely applied to a humid sensor, a gas sensor, an oxygen concentrator, and the like, due to proton conductivity thereof.

[0008]

Particularly, a membrane formed of the fluoropolymer electrolyte membrane typified by the perfluoro sulfonic acid membrane which is known under a trade name of Nafion (manufactured by Du Pont Co., Ltd.), is used as an electrolyte membrane to be used under a severe condition, due to considerably high chemical stability thereof.

[0009]

However, the fluoropolymer electrolyte has shortcomings that it is difficult to produce, and is extremely costly. Therefore, it has been considered that oxidation resistance be enhanced by quenching a hydrogen peroxide radical generated in a system of the hydrocarbon polymer electrolyte membrane.

[0010]

Compared with the fluoropolymer electrolyte membrane typified by Nafion®, the hydrocarbon polymer electrolyte membrane has advantages that it is easy to produce and is low in cost. However, there remains a problem concerning the hydrocarbon polymer electrolyte membrane that oxidation resistance thereof is low, as mentioned above. The low oxidation resistance is due to the facts that a hydrocarbon compound generally has low resistance to a radical, and that an electrolyte having a hydrocarbon skeleton is likely to cause deterioration reaction due to the radical (an oxidation reaction due to a peroxide radical).

[0011]

Therefore, applications describing a high-durability polymer electrolyte (following patent document 1), and a high-durability polymer electrolyte composite (following patent document 2) have been filed in order to provide a high-durability polymer electrolyte which has oxidation resistance that is equal to or higher than that of a fluoropolymer electrolyte or that is sufficient for actual use, and which can be produced at a low cost. The high-durability polymer electrolyte (following patent document 1) is formed of a polymer compound having a hydrocarbon portion. A functional group containing phosphorus is introduced to this high-durability polymer electrolyte. The high-durability polymer electrolyte composite (following patent document 2) is obtained by mixing a polymer compound having an electrolytic functional group and a hydrocarbon portion with a compound containing phosphorus.

[0012]

[Patent Document 1]

Japanese Patent Laid-Open Publication No. 2000-11755

[Patent Document 2]

Japanese Patent Laid-Open Publication No. 2000-11756

[0013]

[PROBLEM TO BE SOLVED BY THE INVENTION]

However, in the case where the hydrocarbon polymer electrolyte membrane is used in the fuel cell, since the antioxidant electrolytes disclosed the above-mentioned patent documents 1 and 2 have high gas impermeability, each of the antioxidant electrolytes greatly hinders fuel gas (hydrogen or the like) or oxidizing gas (oxygen, air, or the like) from contacting a catalyst (platinum or the like), and considerably deteriorates performance of the fuel cell, when being provided in the electrode. As described so far, there exists a problem in the combination of the hydrocarbon polymer electrolyte, and the functional group containing phosphorus or the compound containing phosphorus. In light of the above-described circumstances, it is an object of the invention to create a novel polymer antioxidant which significantly enhances durability of a polymer electrolyte used for a fuel cell or the like.

[0014]

[MEANS FOR SOLVING THE PROBLEM]

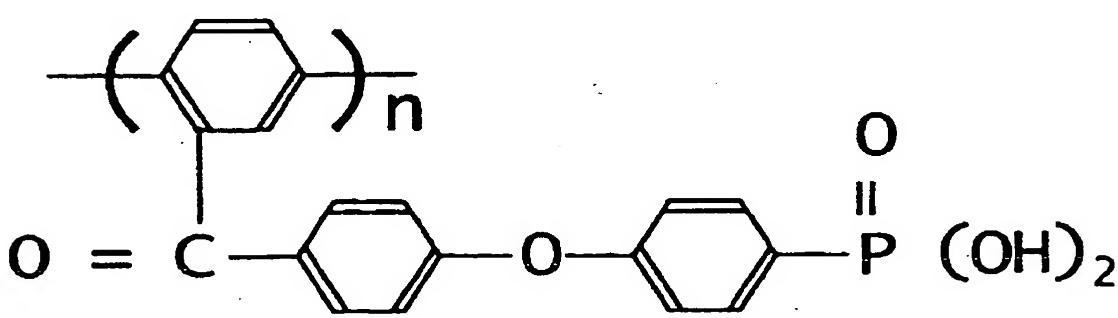
As a result of a dedicated research, the inventors of the present invention have achieved the invention by synthesizing a novel phosphorus-containing polymer compound which is appropriate for an antioxidant that improves oxidation resistance stability of a fluoropolymer electrolyte which originally has relatively high chemical stability.

[0015]

A first aspect of the invention relates to phosphonated poly (4-phenoxybenzoyl-1,4-phenylene) having a following repeating unit.

[0016]

(Chemical formula 5)



(It is to be noted in the above formula that "n" represents a number of 5 to 10000.)

[0017]

By having the main chain be a wholly aromatic chain, the phosphorus-containing polymer compound according to the invention can have high-insolubility and heat resistance compared with a polyvinyl phosphonic acid whose main chain is

an aliphatic chain. More particularly, the polyvinyl phosphonic acid dissolves in water and a thermal decomposition temperature thereof is 180 °C, whereas phosphonated poly (4-phenoxybenzoyl-1,4-phenylene) is insoluble in water, and a thermal decomposition temperature thereof is 350 °C. There is remarkable differences between the polyvinyl phosphonic acid and phosphonated poly (4-phenoxybenzoyl-1,4-phenylene) not only in chemical formulas but also in physical properties.

[0018]

A second aspect of the invention relates to a method for synthesizing phosphonated poly (4-phenoxybenzoyl-1,4-phenylene). In this method, poly (4-phenoxybenzoyl-1,4-phenylene) is used as a starting material, a phenoxy group of the poly (4-phenoxybenzoyl-1,4-phenylene) is halogenated, the halogen group is phosphonic acid esterified, and the phosphonic acid ester group is deesterified.

[0019]

FIG. 1 shows a synthesizing scheme of phosphonated poly (4-phenoxybenzoyl-1,4-phenylene). Poly (4-phenoxybenzoyl-1, 4-phenylene) is used as a starting material (I;PPBP), and a phenoxy group of the of the poly (4-phenoxybenzoyl-1,4-phenylene) is halogenated such that halogenated-poly (4-phenoxybenzoyl-1, 4-phenylene) is obtained (II;X-PPBP). Next, a halogen group of the halogenated-poly (4-phenoxybenzoyl-1, 4-phenylene) is phosphonic acid esterified using phosphonic acid trialkyl such that phosphonic acid esterified poly (4-phenoxybenzoyl-1, 4-phenylene) is obtained (II; EP-PPBP). Finally, a phosphonic aicd ester group of phosphonic acid esterified poly (4-phenoxybenzoyl-1, 4-phenylene) is deesterified such that phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene), which is a desired compound, is obtained (IV; P-PPBP).

[0020]

Although halogen to be used is not particularly limited, it is preferable to use bromine. Although phosphonic acid trialkyl to be used is not particularly limited, it is preferable to use lower alkyl phosphonic acid such as methyl and ethyl.

[0021]

As mentioned above, phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) is insoluble in water, and excels in heat resistance. Accordingly, when being added to various organic materials, phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) effectively functions as an antioxidant. Namely, a third aspect

of the invention relates to an antioxidant formed from phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene).

[0022]

An organic material to which phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) is added as an antioxidant is not particularly limited. Phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) may be added to a natural resin, a synthetic resin, a natural rubber, a synthetic rubber, natural fibers, synthetic fibers and the like.

[0023]

Concrete examples of organic materials are polyolefin resins such as polypropylene resin, polyethylene resin, polybutene resin, and polypentene resin; thermoplastic resins such as polystyrene resin, acrylonitrile-butadiene-styrene resin, polycarbonate resin, polyphenylene ether resin, acrylic resin, polyamide resin, and polyvinyl chloride resin; rubber materials such as natural rubber (NR), isoprene rubber (IR), butadiene rubber (BR), 1,2-polybutadiene rubber (1,2-BR), styrene-butadiene rubber (SBR), chloroprene rubber (CR), nitrile rubber (NBR), butyl rubber (IIR), ethylene-propylene rubber (EPR, EPDM), chlorosulfonated polyethylene, acrylic rubber, epichlorohydrin rubber, polysulfide rubber, silicone rubber, fluorinated rubber, and urethane rubber; and thermosetting resins such as polyurethane, polyisocyanate, polyisocyanurate, phenol resin, epoxy resin, urea resin, melamine resin, unsaturated polyester resin, and polyimide. Each of these materials may be used by itself. Also, two or more of these materials can be used in combination.

[0024]

As described above, phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) according to the invention is added to various organic materials, and effectively functions as the antioxidant. Among the organic materials, when phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) is added to the polymer electrolyte, durability of the polymer electrolyte can be drastically enhanced. Particularly, when phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) is added to the fluoropolymer electrolyte, durability of the polymer electrolyte can be further enhanced. Namely, a fourth aspect of the invention relates to a high-durability polymer electrolyte composite containing a fluoropolymer electrolyte and phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene).

[0025]

Originally, the fluoro high polymer is chemically stable, since inter-molecular bonding between a carbon atom and a fluorine atom is strong. Therefore, it has not been considered that a measure to stabilize the fluoro high polymer should be taken. However, according to findings made by the inventor and et al., even in the fluoro high polymer, when a hydrogen peroxide radical or the like is generated in a system, decomposition of a side chain occurs successively in the unit of fluorine-containing ether. Also, once decomposition starts, since an amount of heat generation is large due to high bond energy between the atoms, thermal decomposition proceeds rapidly.

[0026]

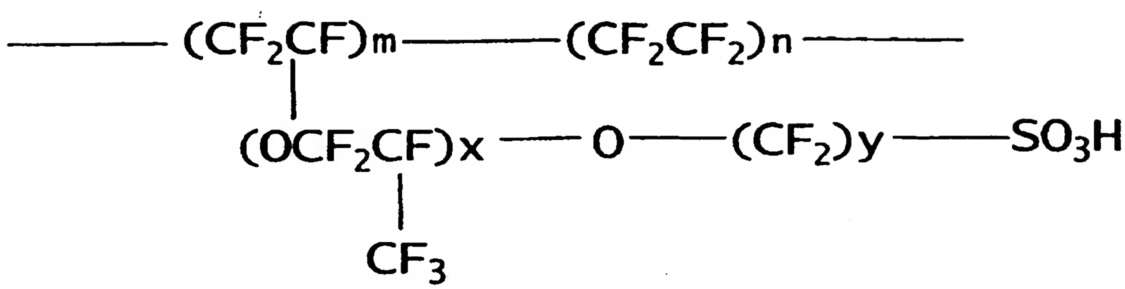
According to the invention, by adding phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) to the fluoropolymer electrolyte as an antioxidant, phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) quenches not only the hydrogen peroxide radical generated in the system but also the decomposition radical generated in the process of decomposing the fluoropolymer electrolyte, thereby improving oxidation resistance stability of the fluoropolymer electrolyte.

[0027]

In the invention, the fluoropolymer electrolyte is a fluoropolymer polymer compound to which an electrolytic functional group such as a sulfonic acid group and a carboxylic acid group is introduced. More particularly, the fluoropolymer electrolyte is a polymer formed by introducing the electrolytic functional group such as the sulfonic acid group as a substituent to a fluorocarbon skeleton or a hydrofluorocarbon skeleton. The fluoropolymer electrolyte may have an ether group, chlorine, a carboxylic acid group, a phosphoric acid group or an aromatic ring in a molecule. Generally, a polymer having perfluorocarbon as a main chain skeleton, and having the sulfonic acid group through a spacer such as perfluoro ether and the aromatic ring is used. Concrete examples are polymers having structures expressed by the following chemical formulas 6 and 7.

[0028]

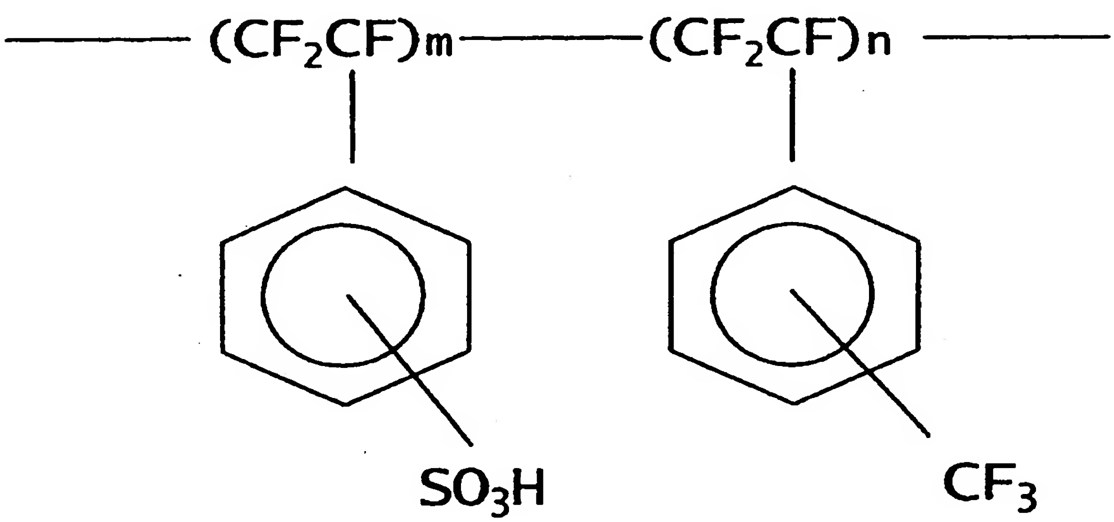
(Chemical formula 6)



(It is to be noted in the above formula that “x” represents an integral number of 0 to 2, “y” represents an integral number of 2 or 3, “n/m” represents a number of 1 to 10.)

[0029]

(Chemical formula 7)



(It is to be noted in the above formula that “n/m” represents a number of 0.1 to 2.)

[0030]

As the polymer expressed by the chemical formula 6, “Nafion ®” manufactured by Du Pont Co., Ltd., “Aciplex-S ®” manufactured by Asahi Chemical Industry Co., Ltd. and the like are known. The above-mentioned patent document 3 discloses that the polymer expressed by the formula 7 is used as a fuel cell. The perfluoropolymer expressed by the formula 6 excels in stability when being used as a fuel cell. Accordingly, it is preferable that the perfluoropolymer expressed by the formula 6 be used as a material to which the invention is applied.

[0031]

A mixture ratio of phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) to the fluoropolymer electrolyte is adjusted according to characteristics required of the polymer electrolyte, such as conductivity and oxidation resistance.

[0032]

Namely, as the percentage of phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP)content increases, oxidation resistance is enhanced. However, since phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) is acidulous, as the content thereof increases, conductivity of the entire material decreases. Accordingly, when phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) is used in a case where only oxidation resistance is required and high conductivity is not required, the mixture ratio of phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) to the high polymer compound containing the fluoropolymer electrolyte is increased.

[0033]

Meanwhile, in the case where both high oxidation resistance and high conductivity are required, such as in a fuel cell and water electrolysis, phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) and a fluoropolymer electrolyte to which a strong acid group such as a sulfonic acid group is introduced are mixed with each other at a predetermined mixture ratio. Meanwhile, in the case where high resistance to chlorine and a high-temperature and concentrated sodium hydroxide solution is required, and back diffusion of ions needs to be prevented, such as in salt electrolysis, phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) and a fluoropolymer electrolyte to which a sulfonic acid group, a carboxylic acid group and the like are introduced are mixed with each other at a predetermined ratio.

[0034]

However, when a percentage of phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) content becomes lower than 0.1 mass % of the entire electrolyte composite, the effect of enhancing oxidation resistance becomes insufficient. Accordingly, the percentage of phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) content needs to be equal to or higher than 0.1 mass % of the entire electrolyte composite. Particularly, in the case of a polymer electrolyte which is to be used under a severe condition, such as in a fuel cell, water electrolysis, and salt electrolysis, it is preferable that the percentage of phosphonated poly (4-

phenoxybenzoyl-1, 4-phenylene) (P-PPBP) content be equal to or higher than 5 mass % of the entire electrolyte composite.

[0035]

As an antioxidant to be added to the fluoropolymer electrolyte composite according to a fourth aspect of the invention, an antioxidant to be added to a known polymer electrolyte can be used in combination with phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP). Examples of the antioxidants are a phenol compound, an amine compound, a sulfur compound, and a compound containing phosphorus.

[0036]

Examples of phenol compounds are hydroquinone, p-cresol, BHT, and a hindered phenol compound. Concrete examples of the hindered phenol compounds are 2,6-di-tert-butyl-4-methylphenol; 2,2'-methylene-bis (4-methyl-6-tert-butylphenol); 2,2'-methylene-bis (4-ethyl-6-tert-butylphenol); 4,4'-thio-bis (3-methyl-6-tert-butylphenol); 4,4'-butylidene-bis (3-methyl-6-tert-butylphenol); triethyleneglycol-bis (3-(3-tert-butyl-5-methyl-4-hydroxyphenyl) propionate); 1,6-hexanediol-bis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate); 2,2-thio-diethylenebis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate); octadecyl-3- (3,5-di-tert-butyl-4-hydroxyphenyl) propionate; 3,5-di-tert-butyl-4-hydroxybenzylphosphonate-diethylester; 1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl)–4hydroxybenzylbenzene; and iso-octyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate.

[0037]

Concrete examples of the amine compounds are phenyl-2-naphthylamine; phenothiazine; diphenylphenylenediamine; naphthylamine; octylated diphenylamine (4,4'-dioctyl-diphenylamine); 4,4'-dicumyl-diphenylamine; 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline; and 2,2,4-trimethyl-1,2-dihydroquinolinepolymer.

[0038]

Concrete examples of the sulfur compounds are 2-mercaptobenzimidazol; and 2,4-bis ((octylthio) methyl)–o-cresol; and 2,4-bis-(n-octylthio)-6-(4-hydroxy-3,5-di-tert-butylanilino)-1,3, 5-triazine.

[0039]

An example of the compound containing phosphorus may be selected from a group consisting of phosphoric acid; triethyl phosphite; triethyl phosphate;

triphenylphosphine; triphenylphosphine oxide; triphenylphosphine sulfide; distearylpentaethyldiphosphite; organic phosphite; diphenylisodecylphosphite; diphenyliso-octylphosphite; diisodecylphenylphosphite; triphenylphosphite; and trisnonylphenylphosphite. It is preferable that an example of the compound containing phosphorus be selected from a group consisting of conjugated organic phosphite; polyphosphite; and tetrapentaerythritol.

[0040]

Among the compound containing phosphorus, it is particularly preferable to use alkyl sulfone. Concrete examples are a polyvinyl phosphonic acid, a xylidyl phosphonic acid, and a benzyl phosphonic acid.

[0041]

It is possible to use one type, or two or more types of the antioxidants in combination with phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP). The percentage of all the antioxidants content is normally 0.005 to 50 mass % of the polymer electrolyte composite, and is preferably 0.01 to 10 mass % of the polymer electrolyte composite.

[0042]

Also, it is possible to use another compound containing phosphorus in combination with phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP). In this case, the compound containing phosphorus is a substance having a functional group containing phosphorus. The compounds containing phosphorus correspond to a compound having a functional group containing phosphorus and a polymer compound having a functional group containing phosphorus in a main chain or a side chain.

[0043]

Concrete examples of the functional group containing phosphorus are a phosphonic acid group, a phosphonic acid ester group, a phosphite group, phosphoric acid, and phosphoric acid ester. Among these functional groups, the phosphonic acid group is particularly appropriate as the functional group containing phosphorus, since the phosphonic acid group is inexpensive, and can provide high oxidation resistance to organic materials.

[0044]

Concrete examples of the phosphorus-containing polymers are polyvinyl phosphonic acid or a polyether sulfonic resin to which the phosphonic acid group or the like is introduced; a polyether ether ketone resin; a straight chain type phenol

formaldehyde resin; a crosslinked phenol formaldehyde resin; a straight chain type polystyrene resin; a crosslinked polystyrene resin; a straight chain type poly (trifluorostyrene) resin; a crosslinked (trifluorostyrene) resin; a poly (2,3-diphenyl-1,4-phenylene oxide) resin; a poly (allylether ketone) resin; a poly (arylene ether sulfone) resin; a poly (phenylquinoxaline) resin; a poly (benzylsilane) resin; a polystyrene-graft-ethylenetetrafluoroethylene resin; a polystyrene-graft-polyvinylidene fluoride resin; and a polystyrene-graft-tetrafluoroethylene resin. Further examples of phosphorus-containing polymer are a polyimidazole containing phophonic acid; a polyacrylo phosphonic acid; and phosphonic acid oligomer containing fluoroalkyl.

[0045]

The method for mixing the fluoropolymer electrolyte and phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) is not particularly limited, and various methods can be employed. For example, doping or blending using a solution may be employed. When both the fluoropolymer electrolyte and the antioxidant dissolve by heat, blending by heat dissolution may be employed.

[0046]

Also, a configuration may be employed in which the antioxidant is dispersed evenly in the polymer electrolyte by mixing the fluoropolymer electrolyte and phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) evenly. Alternatively, a main portion of the polymer electrolyte may be formed only of the fluoropolymer electrolyte, and only a portion which requires oxidation resistance may be formed of the mixture of the fluoropolymer electrolyte and the antioxidant.

[0047]

In a condition where a radical is generated randomly in the membrane, for example, when the polymer electrolyte membrane is heated while being immersed in a peroxide solution, a configuration, in which the fluoropolymer electrolyte and phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) are mixed evenly and phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) is uniformly dispersed in the polymer electrolyte membrane evenly, is effective.

[0048]

Meanwhile, in an environment where a peroxide is generated in a catalyst layer on a surface of an electrolyte membrane such as an electrolyte membrane for water electrolysis or a fuel cell, the generated peroxide becomes a peroxide radical

while being diffused, and causes a deterioration reaction, it is not necessary that phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) be dispersed evenly in the electrolyte membrane. In this case, only a surface portion of the electrolyte membrane where oxidation degradation reaction is the most vigorous is formed of the mixture of the fluoropolymer electrolyte and phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP).

[0049]

A method, whereby a membranous product formed of the mixture of the fluoropolymer electrolyte and phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) is interposed between the electrolyte formed only of the fluoropolymer electrolyte and the electrode, is effective for maintaining the performance of the electrolyte membrane.

[0050]

The high-durability polymer electrolyte composite formed of the fluoropolymer electrolyte and phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) according to the invention can be preferably used for a fuel cell, water electrolysis, hydrohalic acid electrolysis, salt electrolysis, an oxygen concentrator, a moisture sensor, a gas sensor and the like.

[0051]

A fifth aspect of the invention relates to an electrode for a fuel cell, which is formed of a proton exchange material and a catalyst support conductive material. In the electrode for a fuel cell, the high-durability polymer electrolyte composite according to the fourth aspect of the invention is used as the proton exchange material.

[0052]

Thus, even when the peroxide radical is generated under a high heat condition, the radical can be suppressed, and the durability of the fluoropolymer electrolyte is increased. Also, due to the combination of the fluoropolymer electrolyte and the wholly aromatic polymer containing the phosphonic acid group as an antioxidant, (1) since nonsolubility of the antioxidant is high, an outflow to the outside of the system is small even when being used in a humid condition, (2) since phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) is wholly aromatic and heat resistance thereof is high, a decomposition amount is small and the effect of preventing oxidation can be maintained for a long time. In addition, (3) microphase separation

between the materials is promoted. Due to promotion of phase separation, porosity increases. Accordingly, the proton exchange material is prevented from coating the catalyst in the electrode. Due to these effects, the performance of the fuel cell can be maintained for a long time.

[0053]

A sixth aspect of the invention relates to a fuel cell using the electrode for a fuel cell according to a fifth aspect of the invention. More specifically, the fuel cell is formed by bringing the electrode catalyst layer formed by laminating catalyst support bodies into close contact with the polymer electrolyte membrane selectively pervious to a proton (hydrogen ion), and sandwiching the polymer electrolyte membrane between a pair of the electrodes with an electrolyte catalyst layer interposed between each of the electrodes and the polymer electrolyte membrane.

[0054]

[EMBODIMENT OF THE INVENTION]

The embodiment of the invention will be described in more detail.

[Synthesizing phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP)]

As shown in FIG. 2, initially, the end of the side chain of poly (4-phenoxybenzoyl-1, 4-phenylene) (PPBP) was brominated such that brominated poly (4-phenoxybenzoyl-1, 4-phenylene) (Br-PPBP) was obtained. Next, bromine was substituted by a phosphonate ester group such that phosphonic acid esterification poly (4-phenoxybenzoyl-1, 4-phenylene) (EP-PPBP) was obtained. Finally, esterificated phosohonic acid poly (4-phenoxybenzoyl-1, 4-phenylene) (EP-PPBP) was deesterified such that phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) was obtained.

[0055]

Identification of each compound was performed by elemental analysis, ICP, FT-IR, and ^{1}H-NMR. As characteristic evaluations of P-PPBP, a fenton test, a thermal analysis, and conductivity measurement were performed. As shown in FIG. 3, a peak due to C-Br stretching vibration was observed in an FT-IR spectra of Br-PPBP, a peak due to P-O-C stretching vibration was observed in an FT-IR spectra of EP-PPBP, and a peak due to P-O-H stretching vibration was observed in an FT-IR spectra of P-PPBP. According to the results, it was confirmed that the phosphonic acid group was introduced in a para position on a benzene ring of the end of the side

chain of PPBP. By elemental analysis, a bromination rate was calculated to be approximately 100 %, a phosphonic acid esterification rate was calculated to be approximately 64 %, and a phosphonic acidification rate was calculated to be approximately 50 %. Also, it was found that a thermal decomposition temperature of P-PPBP was 350 °C, and P-PPBP showed proton conductivity of approximately $10^{-4}Scm^{-1}$ at 90 % R.H., and 80 °C.

[0056]

[Manufacturing electrode for fuel cell to which phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) is added]

3.3ml of electrolyte solution (a commercial solution containing 5 % of Nafion®), 160 mg of P-PPBP and a predetermined amount of water were added to 1100mg of 60 % platinum support carbon, and they were agitated. A homogeneous dispersive solution was thus made. The dispersive solution was provided on a fluorocarbon resin sheet using a doctor blade, and was dried under a reduced pressure at a temperature of 80 °C for 8 hours. An electrode sheet for a fuel cell is thus obtained. It is to be noted herein that Pt: C: Nafion: P-PPBP = 60:40:28:14.

[0057]

[Decomposition behavior analysis by TG-MS]

An amount of gas generated at each temperature was measured by TG-MS, and an effect on thermal decomposition due to addition of P-PPBP was examined. In an He atmosphere, the temperature increased at a rate of 10°C/min. FIG. 4 shows behaviors of generation of CO_2 and the like, which are the decomposition components of P-PPBP. Only generation of an acetic acid of an adjustment solution origin, and CO_2 and CO of carbon origin were observed near a temperature of 150 °C. Generation of gas of P-PPBP origin was not observed. Decomposition of P-PPBP started from a temperature of 350 °C. This shows that P-PPBP has sufficient heat resistance so as to be able to endure the operating temperature of the fuel cell.

[0058]

According to the above-mentioned results, it was confirmed that the decomposition stability of Nafion® in the electrode for heat was drastically improved due to addition of P-PPBP. The decomposition suppressing mechanism is not exactly clear. However, it can be estimated that successive occurrence of decomposition is stopped by stabilizing the carbon radical after the sulfonic acid group is removed from the polymer electrolyte.

[0059]

[Evaluation of stability with time by cell evaluation]

[Initial characteristics]

An I-V evaluation was performed under conditions of; cell: 80 °C, A (anode) bubbler: H_2, 275cc/min, C (cathode) bubbler: Air, 912cc/min, and both electrodes: 2ata. Although P-PPBP was added to the electrode, an inclination of the example was substantially the same as that of an electrode to which P-PPBP was not added. The example and the comparative example have substantially the same contact resistance between the membrane and the electrode. Also, the example and the comparative example have substantially the same limiting current values, and drainage characteristics of the electrodes. The fact, that the limiting current values are substantially the same although the amount of the electrolyte is increased to 1.5 times in weight, and is increased to approximately two times in volume due to addition of P-PPBP, shows that drainage characteristics are not deteriorated due to addition of P-PPBP. According to the results, it was confirmed that the fuel cell characteristics, particularly resistance and the limiting current value do not change due to addition of P-PPBP.

[0060]

[Gas leak amount measured by acceleration durability test]

Continuous operation was performed under conditions of; cell: 80 °C, A: humidified H_2 gas, C: humidified air, and under load conditions including a condition of open circuit. When P-PPBP was not added, the gas leak amount was increased from the beginning. When P-PPBP was added, the gas leak amount was maintained at a low level even when 250 hours have passed. Originally, the effect of preventing oxidation due to addition of P-PPBP is expected on the electrolyte in the electrode. However, according to the results, it was confirmed that deterioration of the electrolyte membrane was also suppressed. The cause for the phenomenon is not exactly clear. However, it can be considered that the hydrogen peroxide radical or the decomposition radical generated in the electrode was inactivated by the antioxidant, and the disperse of the radical into the electrolyte membrane was suppressed.

[0061]

[EFFECTS OF THE INVENTION]

The novel wholly aromatic polymer containing phosphorus according to the invention has high heat resistance, and useful. Accordingly, the wholly aromatic

polymer containing phosphorus according to the invention can be added to various organic materials as an antioxidant. Especially, even when the hydrogen peroxide radical is generated under a high heat condition, the radical can be quenched, and durability of the fluoropolymer electrolyte is enhanced by combining fluoropolymer electrolyte with the wholly aromatic polymer containing phosphorus. Also, when the invention is applied to a fuel cell, since insolubility of the antioxidant is high, an outflow to the outside of a system is small even in a humid condition, and high heat resistance is maintained for a long time. Porosity increases due to microphase separation between the materials. Accordingly, the proton exchange material is prevented from coating the catalyst in the electrode. Due to these effects, the performance of the fuel cell can be maintained for a long time.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[FIG. 1]

FIG. 1 shows a synthesizing scheme of phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP).

[FIG. 2]

FIG. 2 shows a synthesizing scheme of phosphonated poly (4-phenoxybenzoyl-1, 4-phenylene) (P-PPBP) according to an embodiment of the invention.

[FIG. 3]

FIG. 3 shows FT-IR spectras of Br-PPBP, EP-PPBP, and P-PPBP.

[FIG. 4]

FIG. 4 is a graph showing gas leak amounts of materials to which P-PPBP is added, obtained by an acceleration durability test.

[NAME OF THE DOCUMENT] DRAWINGS

FIG. 1

1. HALOGANATION
2. PHOSPHONIC-ACID-ESTERIFICATION
3. DEESTERIFICATION

FIG. 2

1. ROOM TEMPERATURE

FIG. 3

1. ABSORPTION/a.u
2. WAVE NUMBER/cm^{-1}

FIG. 4

1. GAS GENERATION AMOUNT (ng/g)
2. CO_2 (CARBON ORIGIN)
3. ACETIC ACID (ADJUSTMENT SOLUTION ORIGIN)
4. CO + OTHER (CARBON ORIGIN)
5. ORGANIC GAS
6. TEMPERATURE (°C)

[NAME OF THE DOCUMENT] ABSTRACT OF THE DİSCLOSURE

[ABSTRACT]

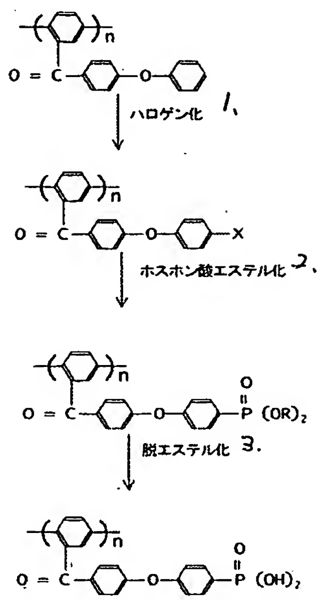
[TASK] To provide a polymer that provides excellent oxidation resistance, for example, to an electrolyte membrane used in a fuel cell, etc., and also provide a high-durability polymer electrolyte composite, and a high-durability fuel cell.

[MEANS OF SOLVING THE PROBLEM]

The invention provides phosphonated poly (4-phenoxybenzoyl-1,4-phenylene), and synthesizing method thereof, an antioxidant formed of phosphonated poly (4-phenoxybenzoyl-1,4-phenylene), a high-durability polymer electrolyte composite formed of a fluoropolymer electrolyte and phosphonated poly (4-phenoxybenzoyl-1,4-phenylene), and a fuel cell in which the high-durability polymer electrolyte composite is used in an electrode thereof.

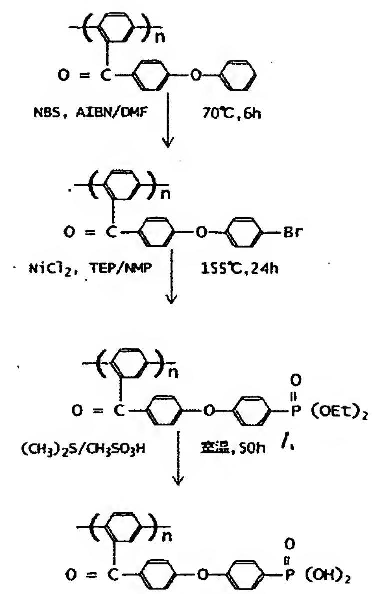
[SELECTED DRAWING] FIG. 1

【図１】



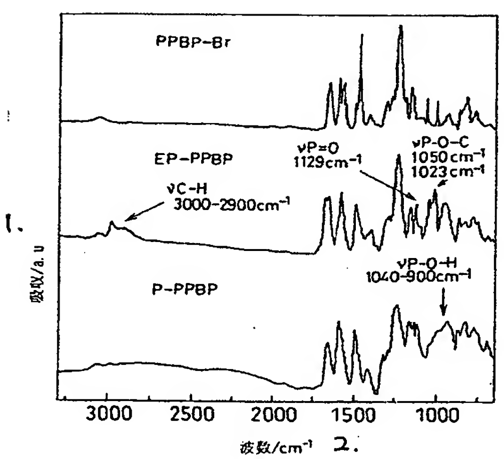
ハロゲン化
ホスホン酸エステル化
脱エステル化
(I)
(II)
(III)
(IV)

【図２】



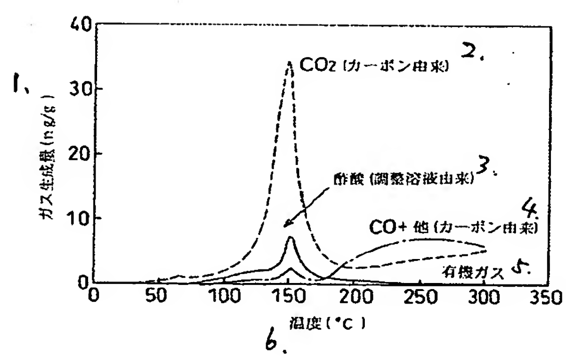
PPBP
NBS, AIBN/DMF
70℃,6h
Br-PPBP
NiCl2, TEP/NMP
155℃,24h
EP-PPBP
(CH3)2S/CH3SO3H
室温,50h
P-PPBP

【図３】



PPBP-Br
EP-PPBP
P-PPBP
νC-H
3000-2900cm-1
νP=O
1129cm-1
νP-O-C
1050cm-1
1023cm-1
νP-O-H
1040-900cm-1
吸収/a.u
波数/cm-1

【図４】



CO2 (カーボン由来)
酢酸 (調整溶液由来)
CO+ 他 (カーボン由来)
有機ガス
ガス生成量 (ng/g)
温度 (°C)